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WHITE OAK LABORATORY

A CHEMICAL MONITORING PROGRAM OF THE EXPLOSION PRODUCTS IN UNDERWATER EXPLOSION TESTS

BY
Ming G. Lai

4 APRIL 1975

NAVAL SURFACE WEAPONS CENTER
WHITE OAK LABORATORY
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A chemical monitoring program of the explosion products in underwater explosion tests is described. The objective of the program is to monitor water quality chemically after underwater explosion tests. The program consists of sampling and preservation of water and sediment samples, separation, concentration,

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20. and determination of various explosion products. General concepts, procedures, and equipment needed for each phase of the program are presented. Guidelines and recommendations for the overall program are also given.

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A CHEMICAL MONITORING PROGRAM OF THE EXPLOSION PRODUCTS IN UNDERWATER EXPLOSION TESTS

The Navy has been conducting underwater explosion tests in fresh waters and marine waters for many years. Although the tests, based on qualitative information, are believed to contribute no adverse effects on the environment, factual data are still needed for the quantitative assessment of the probable environmental impact from the tests. In addition, new explosive compositions have products that may be less acceptable than the products of compositions frequently used in the past. This report has been prepared to institute a chemical monitoring program of the explosion products in underwater explosion tests, to determine monitoring parameters, and to provide procedures and methodology for the program.

Because of the complexity of underwater explosion testing, this report is aimed to serve as a general guide for several common types of explosives used in the tests. Parameters for other specific operations should be further formulated as requirements arise.

In order to specify procedures adequately, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The preparation of this report was sponsored by the Naval Sea Systems Command under Task SEA-SF53554-301 .

JOHN B. WILCOX
By direction

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I

INTRODUCTION

1.1 BACKGROUND

The U. S. Navy is engaged in an intensive effort to minimize or eliminate pollution of all kinds. This overall effort to combat undesirable environmental effects extends to the manufacture and testing of explosives and of weapons. The aspect of the work of concern here is underwater testing, which is vital to the mission of the Navy.

The majority of people with expert knowledge of underwater explosion phenomena believe that the effects of any test on the environment are localized and short-lived and cause no irreversible changes in the general ecology of a natural body of water. Longer range effects are minimal and can be estimated on the basis of existing information, but these estimates are qualitative because most of the previous work has been directed toward the predictions of the early-time, close-in phenomena of military interest.

In order to assess the probable environment impact of the underwater explosion tests, it is necessary to assemble a body of factual information regarding the effects of the tests on the marine environment. Based on this information standards and guidelines can be implemented for future underwater explosion test programs.

1.2 OBJECTIVE AND SCOPE

One of the major effects of an underwater explosion on the environment is the dispersion of the explosion products after the detonation takes place. The ultimate disposition, of course, depends on whether the product is gaseous or a solid, and whether it is readily soluble in water or remains in a particulate form. Since some of the explosion products (described in Section II) are toxic and could produce adverse physiological effects to aquatic life and wildlife, if present in sufficient concentration levels, field surveys are needed to obtain adequate data on biological, chemical, and physical water quality for the determination of the nature and extent of these effects resulted from the underwater explosion tests.

The purpose of this report is to formulate a chemical monitoring program for underwater explosive testing, determine monitoring parameters, and provide information on the methodology involved. The biological and physical monitoring programs will not be included in this report.

1.3 WATER QUALITY MONITORING PROGRAM

Most of the work in water monitoring has been performed by wet chemical analysis. However, in recent years, the combined needs for rapid, frequent, and trace analysis demand increasing use of instrumental methods, preferably those which can be automated and are continuous in operation.

Instruments for water quality monitoring can be classified in many ways. It is convenient to separate them as follows: continuous samplers, semi-continuous samplers, and laboratory analyzers. Continuous sampler instruments measure a constituent or physical parameter on an uninterrupted basis; these instruments may be used in the field or in the laboratory. Semicontinuous samplers measure a pollutant on an interrupted or discrete sample basis; the analysis is then performed on this sample. Semicontinuous sampling analyzers are utilized in both field and laboratory application. Laboratory analyzers ordinarily operate in the laboratory owing to the constraints of operation intervention, operational environment, and fragility or high-maintenance requirements.

Despite the large advances in instrument automation, the majority of water monitoring information is still obtained with manually operated laboratory analyzers. Manual operation implies human involvement to progress from one step in the analysis to another.

All water quality parameters can be monitored with laboratory analyzers. In trace analysis laboratory analyzers offer better sensitivity and accuracy. In addition, the overall cost of analysis is generally lower.

In view of these advantages, laboratory analyzers are recommended for the water monitoring system in the explosive testing program. Figure 1 shows a sequence of steps for the laboratory instrumental system.

II

EXPLOSION PRODUCTS

A considerable amount of knowledge has been acquired concerning the chemistry of explosives and the shock wave and bubble phenomena of underwater explosions, but only limited attention has been given to the dispersion of the explosion products after the detonation takes place. The ultimate disposition, of course, depends on whether the product is gaseous or a solid, and whether it is readily soluble in water or remains in a particulate form. The size of the pool containing the explosion products depends on the charge weight of the explosive used, and the distribution of explosion products depends on the maximum bubble radius and the depth of the explosion. Most of these phenomena have been discussed in detail in a publication by Yount.[1]

In this section, a brief summary of the explosion products involved in the monitoring program is given. Only the chemical products of a bare explosive charge will be discussed. Materials from the case, fuzing mechanism, and any other detonation devices will not be considered, as they probably bear no major significance to the impact of pollution.

2.1 PHYSICAL FORMS

2.1.1 Gases

The majority of the explosion products are in the form of gases. Initially, the products are contained in a large spherical bubble that pulsates and migrates toward the surface. Most of the gaseous

[1] Young, G. A., "The Physical Effects of Conventional Explosions on the Ocean Environment", Naval Ordnance Laboratory, NOLTR 71-120 3 Aug 1971.

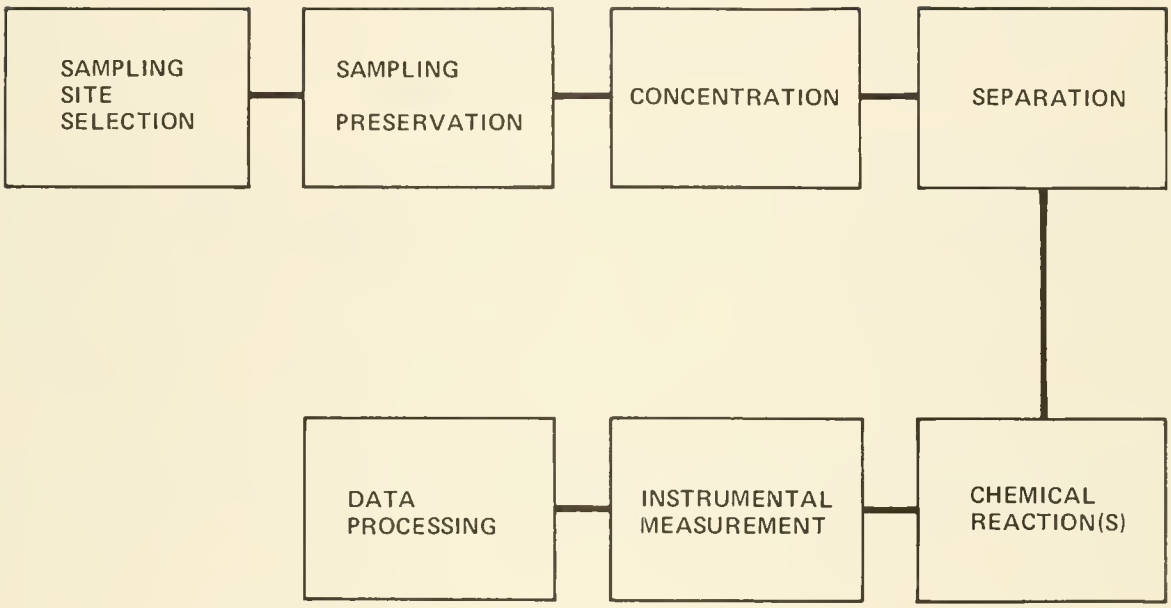

FIG.1 SEQUENCE OF STEPS FOR LABORATORY INSTRUMENTAL SYSTEM FOR WATER QUALITY MONITORING

products will escape to the atmosphere unless an explosion is exceptionally deep, but some are soluble in the water. Only the soluble gases will be considered in this report, since they present a more significant impact to the marine environment.

2.1.2 Suspended Solids

The insoluble solids or particulates are formed during the explosion either by the oxidation of the inorganic components in the explosive mixture or by the reduction of the organic components. The resulting oxides and carbon exist either as fine particulates or colloid, which may remain suspended in the water for an indefinite period of time.

The unconsumed explosives, which are generally insoluble in water, also can disperse in the water as suspended solids. In addition, after the explosion some of the finer bottom particles will be carried upward with the bubbles. It also seems likely that a turbidity cloud of disturbed bottom material will remain in the vicinity of the burst for some period of time. This material would be mixed with the carbon or other particulate explosion products in the surface pool.

2.1.3 Sediment

The solid explosion products together with the bottom particles will begin to settle after the explosion and finally deposit on the bottom in the vicinity of the explosion area. In the case of a deep explosion on a rigid bottom, the bubble tends to pulsate at the bottom before it floats upward. It seems likely that a portion of the solid products will remain in the crater created by the explosion. Most of the particulates will also eventually settle to the bottom. Therefore, an accumulation of the solid explosion products in the sediment near the explosion area is likely.

2.1.4 Dissolved Constituents

The soluble explosion products will dissolve in the water immediately after the explosion. Solutions are usually defined in water chemistry as any chemical species which pass through a 0.45μ membrane filter. Therefore, the dissolved constituents can be easily separated from the suspended solids by the filtration of the mixture through a 0.45μ membrane filter. The soluble species exist as ionic or complex forms in the solution. Some of them will undergo hydrolysis to form colloids.

2.2 CHEMICAL COMPOSITIONS

The explosives most commonly used for underwater explosions are organic nitrated compounds with a chemical formula of the type (C-H-N-O) such as TNT, HMX, RDX, Tetryl, and PETN.[2] Currently several new explosives are also being used in Navy programs. These explosives consist of mixtures of different organic explosives or mixtures of these with metallic components.

In this section the chemical composition of the explosion products from several explosives listed above will be discussed. Information on other specific explosives may be found in the literature.

2.2.1 Dissolved Gases

The gases formed by several explosives are presented in Tables 1 & 2.[3] All the gases are soluble in water at various degrees. The solubility depends on the temperature, pH, and salinity of the water. It is possible that the concentrations of gases in water may temporarily exceed their solubilities. This supersaturation creates excessive total dissolved gas pressure causing undesirable effect to the marine life.

Most of the gases in the explosion products are considered non-toxic, except carbon monoxide (CO), hydrogen cyanide (HCN), chlorine (Cl_2), and ammonia (NH_3), which produce adverse effects to marine life even at low concentrations.

2.2.2 Suspended Solids

Many explosive compositions currently in use consist of metallic compounds. For example, aluminum is frequently incorporated into HBX-1, resulting in the formation of aluminum oxide (Al_2O_3) particles. Zr M-4 contains zirconium metal and lead nitrate which form zirconium oxide (ZrO_2) and lead oxide (PbO) after the explosion. Carbon particles are the major suspended solid after a TNT explosion,

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[2]Cole, R. H., "Underwater Explosions", Princeton University Press, Princeton, New Jersey, 1948.

[3]Young, G. A., "Guide-Line for Evaluating the Environmental Effects of Underwater Explosion Tests", Naval Ordnance Laboratory, NOLTR 72-211, 13 Feb 1973.

TABLE 1

GASEOUS PRODUCTS OF CONFINED EXPLOSIONS
(values in percentage by weight)

Product		Explosives		
Name	Symbol	PETN	HMX	TNT
Carbon Dioxide	CO_2	46.22	28.53	24.22
Carbon Monoxide	CO	14.26	10.02	24.42
Nitrogen	N_2	17.28	34.81	16.28
Water	H_2O	20.97	19.34	12.69
Hydrogen	H_2	0.22	0.20	0.41
Ammonia	NH_3	0.30	3.42	1.21
Methane	CH_4	0.02	0.21	0.70
Hydrogen Cyanide	HCN	-	0.07	0.24
Ethane	C_2H_6	-	0.01	0.05

TABLE 2

TNT PRODUCTS IN A SURFACE POOL

Product		Concentration (mg/l)	
Name	Symbol	Pool	Ocean
Carbon Dioxide	CO_2	0.215	0.631
Carbon Monoxide	CO	0.217	28.8×10^{-6}
Carbon	C	0.172	28
Nitrogen	N_2	0.145	14.3
Water	H_2O	0.113	-
Hydrogen	H_2	3.64×10^{-3}	-
Ammonia	NH_3	1.08×10^{-2}	-
Methane	CH_4	6.22×10^{-3}	40.9×10^{-6}
Hydrogen Cyanide	HCN	2.13×10^{-3}	-
Ethane	C_2H_6	4.44×10^{-4}	1.49×10^{-6}

remaining visible in a surface pool of blackened water. The unconsumed explosives which are insoluble in water, can also disperse in the pool as suspended solids.

Although the disturbed bottom material is part of the suspended solids generated during the explosion, it will not be considered chemically as an explosion product because it does not originate from the explosive.

2.2.3 Sediment

The chemical composition of the explosion products in the sediment will be similar to that of the suspended solids in water. The concentrations, however, are expected to be higher because of localization and accumulation. The amount of solid explosion products deposited on the bottom depends on particle size of the solids, water current, physical characteristics of the sediment, and the depth of the explosion.[3]

2.2.4 Dissolved Constituents

Some of the other explosion products are soluble in water. In PBXW-104, 15% hydrochloric acid (HCl) is produced during the explosion, and HCl is readily soluble in water. Other soluble explosion products include nitrates, perchlorates, chlorides, and a complex of metallic ions such as Al, Pb, Zr, Li, and Hg, which are incorporated in various explosive compositions.

Most of the explosives have low solubilities in water; therefore, the concentration of soluble explosives after the explosion are expected to be small. The toxicity levels of various explosives in water are currently being investigated.

III

SAMPLING AND PRESERVATION

3.1 WATER SAMPLING

3.1.1 General Concepts of Water Sampling

There is no universal procedure for sampling applicable to all

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[3]Young, G. A., op cit, pg 9

kinds of natural waters. The most important requirements for a satisfactory sample are that it be both valid and representative. For a sample to be valid, it has to be one which has been collected by a process of random selection. Any method of sampling that sacrifices random selection will impair statistical evaluation of the analytical data.

A satisfactory sample is not only randomly drawn, but also is representative. This means that the composition of the sample should be identical to that of the water from which it was collected; the collected sample should have the same physiochemical characteristics as the sampled water at the time and site of sampling.

Planning for a sampling program should be guided by the overall objectives of analysis. Major factors of concern for any sampling program are: (a) frequency of sample collection, (b) total number of samples, (c) size of each sample, (d) sites of sample collection, (e) method of sample collection, (f) data to be collected with each sample, and (g) transportation and care of samples prior to analysis.

Frequency of sampling will depend to a large extent upon the frequency of variations in composition of the water to be sampled. There are two principle types of sampling procedures commonly used for analysis of natural waters. The first type is that which yields instantaneous spot or grab samples, while the second type yields integrated continuous or composite samples. A grab sample is a discrete portion of water taken at a given time; a series of grab samples reflects variations in constituents over a period of time. The size of such individual samples will depend on the objectives and methods of analysis, and on the required accuracy. The total number of grab samples should satisfy the statistical requirements of the sampling program.

Composite samples are useful for determining average conditions. A composite sample is essentially a weighted series of grab samples, the volume of each being proportional to the rate of flow of the water at the time and site of sample collection. Samples may be obtained over any time period such as 4, 8, or 24 hours, depending the purposes of analysis.

Selection of sampling sites should be made with great care. A field survey is often useful in planning for site selection. Special consideration should be given to sources of discharge, dilution by tributaries, and changes in surrounding topography.

Sampling can be accomplished by either manual or automatic means, again depending on the purpose or analysis and method of sampling. A grab sample is usually collected manually. When it is necessary to extend sampling over a considerable period of time, or when a continuous (repetitive) record of analysis at a given sampling point is required, automatic sampling equipment is commonly used.

The maintenance of a complete record regarding the source of the sample and the condition under which it has been collected is an inherent part of a good sampling program. This is of particular importance in field or river surveys, where a great number of samples are collected from different sources and under variable conditions. The U.S. Geological Survey has defined the minimum data required for samples of surface waters as follows[4]:

Name of water body
Location of station or site
Point of collection
Date of collection
Time of collection
Temperature of the water
Name of collector
Weather and other natural or other man-made factors that may assist in interpreting the chemical quality

3.1.2 Sampling Techniques

Various techniques have been developed by oceanographers for sampling waters of the seas at various depths. These include, for example, the Nansen bottle, the Niskin bottle, and the Van Dorn Sample (described in 3.1.3). However, sampling of the sub-surface water affected by an explosion would require accurate placement and control of sampling devices and would also involve an appreciable number of stations to insure success. In addition, it would be necessary to employ a sensitive tracer to provide assurance that a sample was, in reality, affected by the explosion.

Several types of tracers have been used during the past for monitoring purposes. Chemical tracers, such as lithium chloride and

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[4]U.S. Department of Public Works, Public Work 85, 1954.

cobalt chloride, were incorporated in an explosive charge of TNT.[5] The amount of tracer in the water samples was analyzed chemically.

Radioactive tracers were employed in the HYDRA-IIA series sponsored by the Naval Radiological Defense Laboratory during the early 60's. The radioactive tracers used on HYDRA-IIA were Lutetium-177 and Xenon-133, which provided excellent results in following the history of the explosion products, because extremely low concentrations of radioactive materials are detectable. The disadvantages of using radioactive tracers are (1) difficulty in handling due to high level of radiation, (2) a source of pollution affecting the marine environment, and (3) relatively expensive.

Fluorescent dyes are used frequently by oceanographers for the study of diffusion processes and as tracers for sewage and other pollutants. They do not have the undesirable features of radioactive tracers. A container of fluorescein dye, mixed with water, can be attached to the supporting cable directly above the charge. A ratio of one lb of dye to 100 lb of explosive should provide visibility for at least one-half hour.[3]

With the help of the tracers, sampling can be done by locating the pool and traversing it with a small boat. If the approximate location of the pool can be predicted beforehand, an array of fixed sampling stations can also be set up before the explosion. Samples can then be collected at a time sequence and at various depths.

Dye concentration can be measured in-situ or in sampling bottles with a fluorometer. Dye concentration can also be determined from an aerial photographic negative with a photodensitometer.[6] This method has the advantage of providing data for the entire surface pool at selected times.

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[3]Young, G. A., op cit, pg 9

[5]Young, G. A., "Effects of the Explosion of 45 Tons of TNT Under Water at a Depth Scaled to Test Baker", Naval Ordnance Laboratory, NAVORD Report 2891, 1953.

[6]Ichiye, T. and Plutchak, N. B., "Photodensitometric Measurement of Dye Concentration in the Ocean", Limnology and Oceanography, 11, No. 3, 364 (1966).

3.1.3 Samplers

The essential requisite of a satisfactory water sampler is that it should capture a truly representative sample of the water at the sampling depth and bring it to the surface unaltered. This necessitates rapid filling with the water surrounding it when open, and perfect sealing when closed. The interior of the sampler should be resistant to corrosion and should not contaminate the sample. Where serial sampling is to be carried out at various depths, it is advantageous for the sampler to be light in weight so that sampling can be carried out over the normal range of depth with one cast.

There are at least two dozen different water sampling bottles in major use, each serving a particular purpose. Bottles are usually opened in-situ by means of weights, or messengers, dropped down the supporting hydrographic wire. Owing to the danger of contamination, metallic samplers should not be used if samples are to be analyzed for trace metals. For such work, the use of plastic water bottles is essential.

Three types of sampling bottles are recommended here:

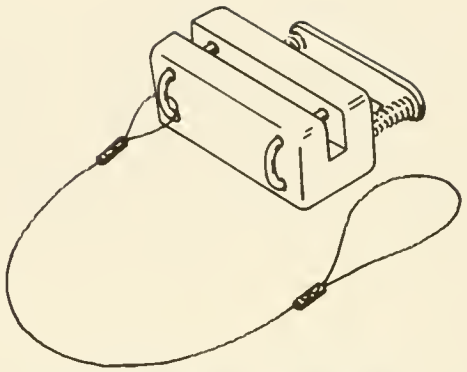
(1) Van Dorn Water Sampler Model XRB-13
(Hydro Products, San Diego, California) - Fig. 2

Specifications

Sample size:	3 liters
OD of sample tube:	5.5 inches
Length of sampler:	12 inches
Weight in air:	5 3/4 lbs
Weight in water:	2 lbs
Weight with sample:	15 lbs
Price	$175

The Hydro Products XRB series water sampler design is an improved version of the classic Van Dorn design. The main body of the sampler is a chemically inert, rugged PVC tube which offers free flushing feature to assure that the water sample is that of the particular depth at which it was triggered, not a mixture of surface and intermediate waters.

Operation is a one-operator job, even in rough waters. The sampler can be rapidly affixed to a hydrographic wire. The unit is cocked using a fast, simple operation. When the sampler is triggered by a messenger at a desired depth, the PVC end caps are released and



HYDROGRAPHIC MESSENGER

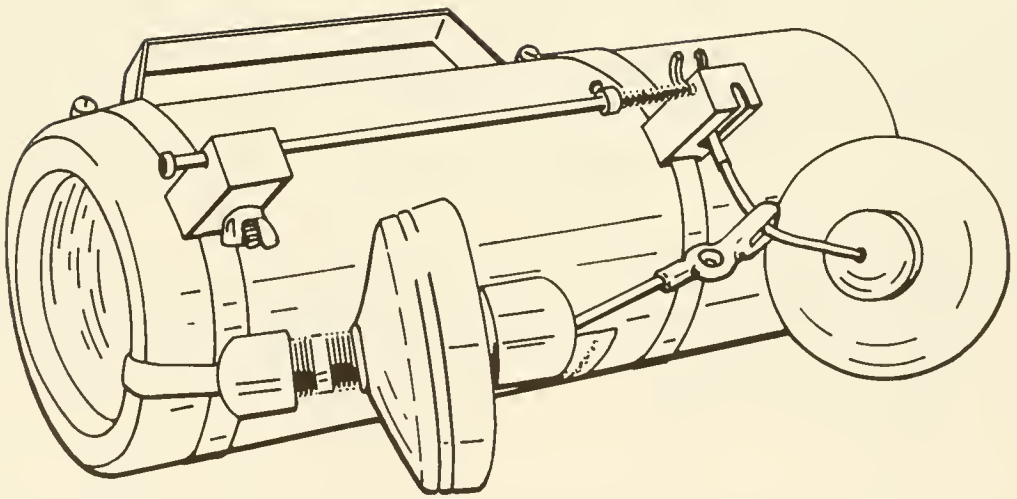


FIG. 2 VAN DORN WATER SAMPLER

snap snugly into the angled end faces on the end of the sample tube. After removal from the wire, the water sample can be drained from the valves to other containers for analysis.

(2) Nonmetallic Niskin Water Sampler Model 1010-1.7 (General Oceanics, Miami, Florida) - Fig. 3

Specifications

Capacity:	1.7 liters
Overall length:	25 inches
Outside diameter:	3.5 inches
Empty weight:	5.3 lbs
Full weight:	9 lbs
Price:	$180

The General Oceanics Model 1010 Niskin Sampling Bottles are general purpose, nonmetallic water samplers suitable for a wide range of oceanic and inland water sampling applications. The bottle features all plastic (PVC or polycarbonate) construction and a free flushing design to yield samples with greater purity and lower self-contamination than those taken with traditional metal bottles.

For on-wire operation, the bottle end stoppers are held open by a cocked trigger mechanism until the bottle has been lowered to the desired depth. A messenger dropped down the wire from the surface, strikes the trigger mechanism and releases the end stoppers for closure. The bottles are designed to release a second messenter down the wire below the bottle to actuate a series of bottles along the wire with a single messenger dropped from the surface. Water may be drained from the bottles by opening an O-ring-sealed, non-metallic stopcock at the lower end. The stopcocks are designed to accept rubber tubing in order that samples may be drawn off with minimal exposure. Reversing thermometer assemblies are available as standard accessories.

(3) Kemmerer Plus Nonmetallic Water Sampling Bottles (Wildco Wildlife Supply Co., Saginaw, Michigan) - Fig. 4

Specifications

Full weight:	14 lbs
Sample volume:	3.2 liters
Overall length:	27 inches
Outside diameter:	4.5 inches
Empty weight:	6 lbs
Price:	$175

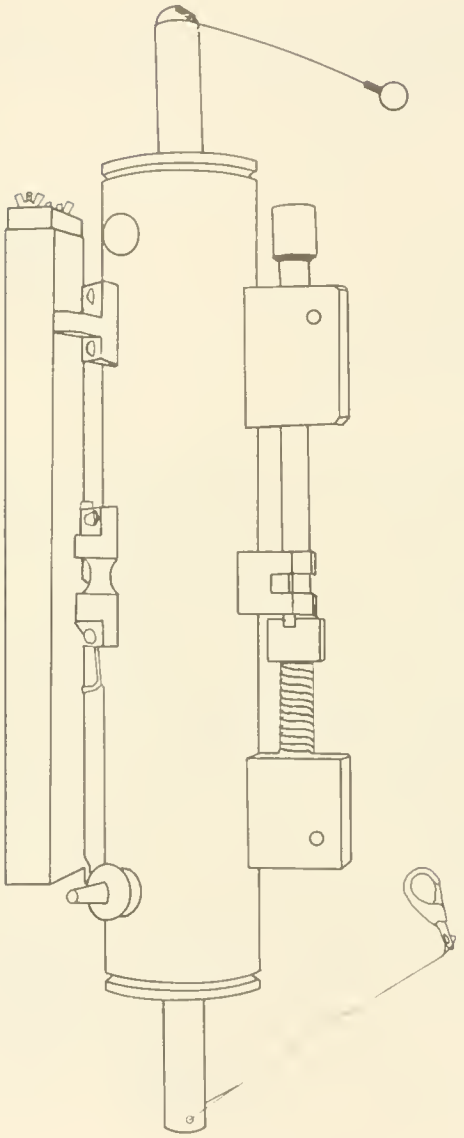


FIG. 3 NON-METALLIC NISKIN WATER SAMPLER

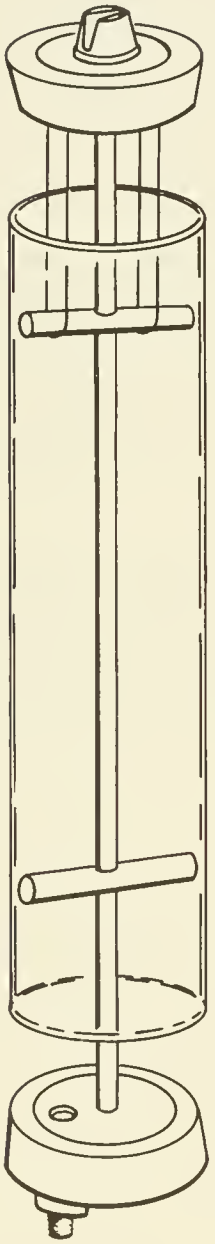


FIG. 4 NON-METALLIC KEMMERER PLUS WATER SAMPLER

The Kemmerer Plus Nonmetallic Bottles are specially designed for trace metal sampling and pesticides or chlorinated hydrocarbon sampling. This is accomplished by constructing the Kemmerer Plus bottle out of materials that cannot contaminate the sample for the types of sampling. Specifically the rubber end seals, valve washer, and the closer have been constructed of materials which will not release trace metal ions or chlorinated hydrocarbons to the sample.

The unique Kemmerer design assures complete flushing of the bottle as it is lowered into the water. Closing of the Kemmerer causes much less agitation disturbance of the sample than the Van Dorn design. Utilizing a specially designed automatic locking device, the stoppers are locked open before the unit is lowered into the water. The valves are closed by dropping a messenger. A drain in the bottom stopper allows the water contained in the sampler to be drawn off for analysis.

For use on explosion tests, special arrangements are required. One approach that has been used successfully is to place a sampler just below the surface at a downstream distance where the explosive effects are not damaging. A dye tracer is added to the explosive and the movement of the surface pool is observed visually. The sampler is activated by wire when the pool arrives. The events are recorded photographically.

3.1.4 Filtration of Water Samples

Natural water contains two principle types of suspended matter (i) inorganic particulate matter resulting from rock weathering and from precipitation, and (ii) marine organisms, their decomposition products and other organic detritus. In explosion tests, particulates such as aluminum oxide particles, unconsumed explosives, and carbon are generated. Since trace metals and organic components from the explosion products can be liberated rapidly from, or be taken up by particulate matter, it is advisable to separate the particular matter immediately after collection.

The suspended matter, after it is separated from water samples, can be saved and analyzed. The separation may be carried out either by centrifugation, or more conveniently, by filtration.

In the selection of a filtering medium the following criteria should be satisfied.

(1) The filter should have a reproducible and uniform pore size. The most commonly used pore size is 0.45μ.

(2) The rate of filtration should be high, and the filter should not clog easily.

(3) The suspended matter should not penetrate into the filter, but should be retained on its surface, so that it can be readily recovered.

(4) The filter should not absorb trace elements.

(5) In order to prevent contamination of the water sample, it should have a low ash content. This also enables the inorganic components of the suspended matter to be recovered by ignition or wet ashing with minimum contamination.

(6) It should contain no loose fibers since these may contaminate the water or suspended matter.

The most satisfactory type of filter for the filtration of water samples for analytical purpose is the molecular membrane filters. These filters are composed of incompletely cross-linked high polymers of partially substituted cellulose acetate and cellulose nitrate, and are approximately 0.15 mm in thickness. They are commercially available in pore sizes ranging from 10 mμ - 5.0μ (Millipore Corporation Inc., Bedford, Massachusetts). The pore sizes show a high degree of uniformity. There is little interconnection of adjacent pore channels, and the pore volume is about 80% of the total volume of the filter, thus allowing a very high rate of filtration. The ash weight of the filters is extremely small and amounts to only 0.0001% of the original weight. Filtration is carried out with suction. A low-cost, hand operated vacuum/pressure pump (Cole-Parmer Instrument Co., Chicago, Illinois) is suitable for field operation. The filter must be supported on a sinstered glass plate or a fritted teflon support. A filtration apparatus of this type is available from Wildco Wildlife Supply Co., Saginaw, Michigan.

3.1.5 Storage of Water Samples

One of the most important aspects of the sampling process is the care and preservation of the sample prior to analysis. A water analysis is of limited value if the sample has undergone physiochemical or biochemical changes during transportation or storage. These changes are time dependent, but they usually proceed slowly. In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results.

Although it is obviously desirable to analyze water samples immediately after collection, this is not always possible, either because of shortage of time or because of lack of facilities on board ship. Rapid changes may occur in the concentrations of micro-components and trace elements unless measures are taken to stabilize them, and to prevent contamination arising from the storage vessel.

In the storage of water samples for trace element analysis, it is necessary to guard against contamination and against losses cause by adsorption. Contamination by the element to be determined may arise by solution or desorption from the walls of the storage container. Contamination arising from the storage vessel is particularly serious if soft glass bottles are used, but may also be appreciable even with borosilicate glass. Polyethylene has been demonstrated to contain extremely low concentrations of trace elements[7], and at present, must be considered the best container material. (Teflon has slightly lower concentration of most trace elements but is very expensive). The risk of contamination of samples by polyethylene containers is generally small, but it is important that new bottles should be treated with diluted hydrochloric acid to remove traces of metals left during the manufacturing process.

Very serious losses of trace elements can occur through adsorption onto the walls of the container.[8] Glass and most plastics are supercooled liquids, which, because of their distorted and broken bonds, have greater surface energy than crystalline substances. This leads to the adsorption of ions from solution and to the formation of bonds between the surface and the absorbed ions. The loss is likely to be greatest with transition elements and with elements which are hydrolysed at pH 7-9, such as iron. Generally, acidification of the sample prevents, or reduces adsorption of trace elements by the container. It will often be found that acidified samples (at a pH value of 1.5) can be stored for several months in polyethylene bottles without change. Before any type of container is used for the storage of samples for trace element analysis, it should be tested to determine whether it adsorbs the element under examination.

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[7]Robertson, D. E., "Role of Contamination in Trace Element Analysis of Sea Water", Anal. Chem. 40, 1067 (1968).

[8]Robertson, D. E., "The Adsorption of Trace Elements in Sea Water on Various Container Surfaces", Anal. Chem. Acta, 42, 553 (1968).

Little is known about the preservation of water samples which are to be analyzed for their organic content. Water samples are generally either acidified to pH 1 or stored in a refrigerator. The samples must be stored in glass bottles since appreciable amounts of organic material can be dissolved from polyethylene.

Changes in temperature and pressure may result in the escape of certain gaseous constituents (e.g. O_2, CO_2, CH_4) or the dissolution of some atmospheric gases. Polyethylene vessels should not be used for storage of such samples on account of their permeability to gases. Weimer[9] found that the method of sample collection and storage greatly affected the reproducibility of the concentration of dissolved methane. Samples stored in 250-ml, glass-stoppered reagent bottles gave variable results. Because of the poor reproducibility obtained with this storage method, a dissolved gas sampling bottle was designed[10] to eliminate contact of the water sample with the atmosphere after the initial sample collection was completed. The dissolved gas sampling bottle is shown in Fig. 5.

Water from a water sampler is added through the neck of the dissolved gas sampling bottle; three bottle volumes are first allowed to flush through the neck and the stopcock. The stopcock is closed, allowing water to fill completely the neck of the bottle. The plunger is inserted (about 0.5-1 inches into the neck) with the stopcock of the bottle open to expel some of the water from the exit post. The stopcock is then closed. The dissolved gas sampling bottle is fitted with a Male Leur tip at the stopcock for the introduction of the water sample into a gas stripping chamber.

3.2 SEDIMENT SAMPLING

3.2.1 General Concepts of Sediment Sampling

The same philosophy and practice applied to water sampling should also be applied to sediment sampling. However, sediment

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[9]Weimer, W. C., "Some Considerations of the Chemical Limnology of Lake Mary, Vilas County, Wisconsin", M.S. Thesis, Water Chemistry Program, University of Wisconsin, Madison, Wis., 1970.

[10]Weimer, W. C. and Lee, G. F., "Method for the Storage of Samples for Dissolved Gas Analysis," Environ. Sci. Technol. 5, 1136 (1971).

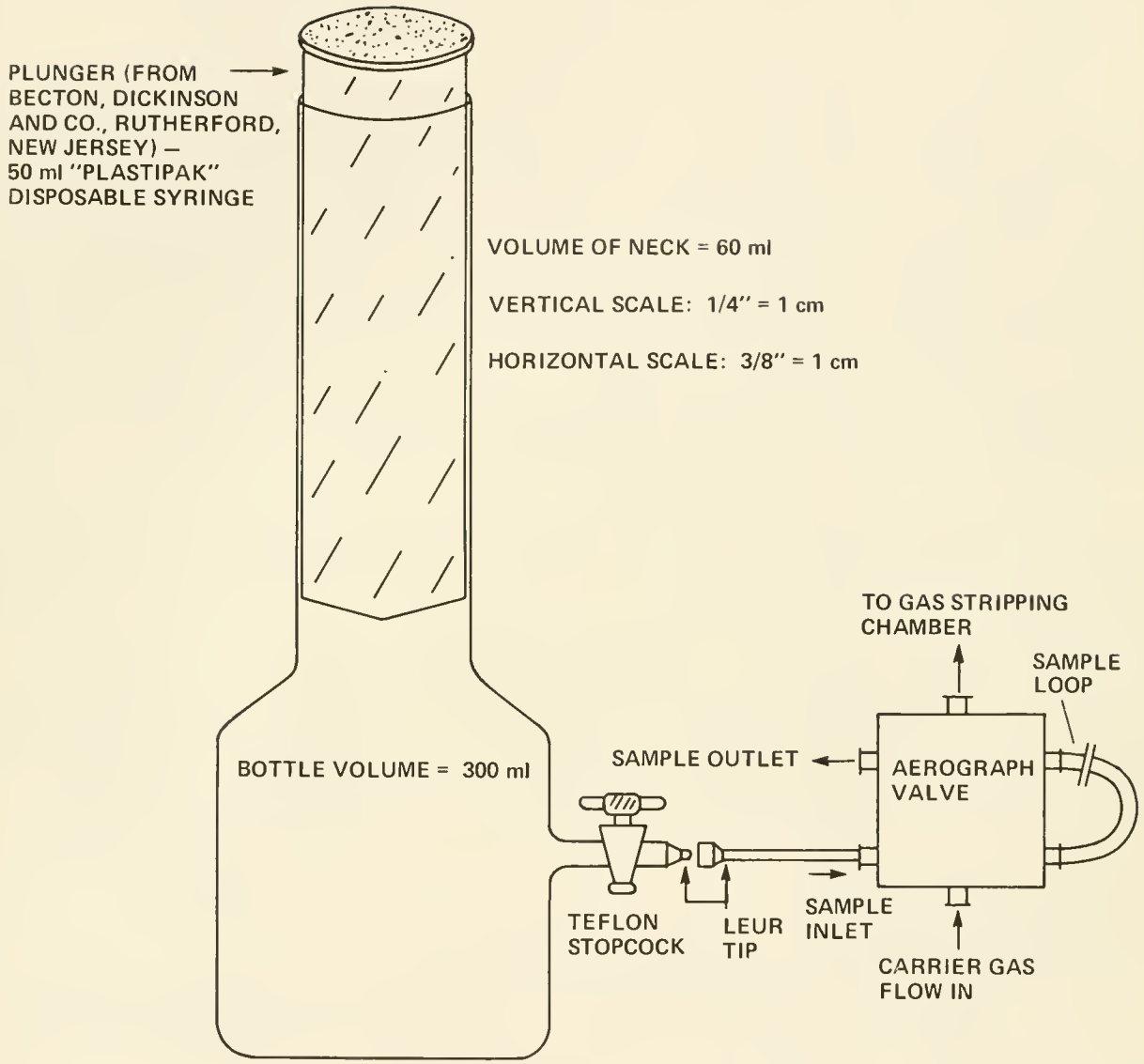
PLUNGER (FROM BECTON, DICKINSON AND CO., RUTHERFORD, NEW JERSEY) — 50 ml "PLASTIPAK" DISPOSABLE SYRINGE
VOLUME OF NECK = 60 ml
VERTICAL SCALE: 1/4" = 1 cm
HORIZONTAL SCALE: 3/8" = 1 cm
TO GAS STRIPPING CHAMBER
SAMPLE LOOP
SAMPLE OUTLET
AEROGRAPH VALVE
BOTTLE VOLUME = 300 ml
TEFLON STOPCOCK
LEUR TIP
SAMPLE INLET
CARRIER GAS FLOW IN

FIG. 5 DISSOLVED GAS SAMPLING BOTTLE

sampling in reality is much more complicated than water sampling because of the following reasons:

(1) Sediment sampling is performed at or near the bottom of the sampling site, which may be deep and inaccessible. Sampling requires elaborate and heavy equipment.

(2) Sediment is composed of various types of material with a large size distribution range. Representative samples are difficult to obtain.

(3) Sediment sampling requires tedious steps in sample processing and handling, such as extracting residual moisture from core samples, transferring samples from samplers to storage containers, and preserving samples at freezing temperature. Contamination and loss of samples may occur if they are not handled properly.

3.2.2 Sampling Techniques

There are three types of sediment sampling, each one serving a particular purpose:

(1) Suspended-sediment sampling - The purpose of the suspended-sediment sampling is to obtain a sampling that is representative of the water-sediment mixture moving in the vicinity of the bottom. The sample can be collected with a Van Dorn water sampler (Section 3.1.3). The sediment is separated from the water by centrifugation, and the sample is transferred into a glass container for storage before analysis.

(2) Grab sediment sampling - Grab sampling of the sediment is performed by grab samplers which usually have the distinctive feature of the shapes of an orange-peel or a clamshell. During sampling, the sampler is lowered to the bottom with its grab opened. The grab is closed after being triggered by electrical or hydraulic means, after closure the sampler is lifted to the surface. The sediment sample is a composite sample of a several inch layer of sediment.

(3) Core sampling - Cylindrical and box corers are used to remove a vertical tube of sediment at a particular location in as undisturbed a state as possible. The purpose may be to examine the historical formation, the interrelationship of the biological components and their environment, or the accumulation of polluted materials from a particular source. These extractive devices can be subdivided by the means utilized in forcing the penetration of

the medium: (1) gravity (weight or hydraulic piston), (2) vibrator (pneumatic and electric), (3) explosive (chemical and electric spark), (4) rotary (hydraulic and direct mechanical), and (5) scuba divers inserting cores by hand. Among them, the gravity corer is most commonly used for general purpose sampling.

The sediment cores collected are immediately extruded and sliced into sections. Each section is squeezed to remove residual water and stored in appropriate containers (Section 3.1.5).

3.2.3 Samplers

There are close to one-hundred different sediment samplers commercially available with price ranging from $30 to $4,000. Many are designed for specific purposes. Others can be used for general purposes. Since there is no "ideal" sampler, selection of an appropriate sampler must depend on the requirements of the program. Considerations should be given to:

1. Types of sediment to be sampled.
2. Depth of the water above the sampling site.
3. Importance of undisturbed, unwashed samples.
4. Introduction of contaminant to the samples.
5. Size and weight of the samples.
6. Requirements for support equipment on board ship.
7. Ease of removal of the sample from the unit.
8. Cost of the unit.

Three types of sediment samplers are recommended for the explosive testing program:

(1) Van Dorn Sampler - Van Dorn sampler, normally used as a water sampler, can be used for sampling suspended and unconsolidated sediment. The description of the Van Dorn sampler is presented in Section 3.1.3.

(2) Shipek Sediment Sampler, Model 860 (Hydro Products, San Diego, California) - Fig. 6

Specifications

Size:	18.6 in. x 17.4 in. x 25.1 in.
Weight:	134 lbs
Materials:	Sampler: cast iron
	Springs: tempered stainless steel

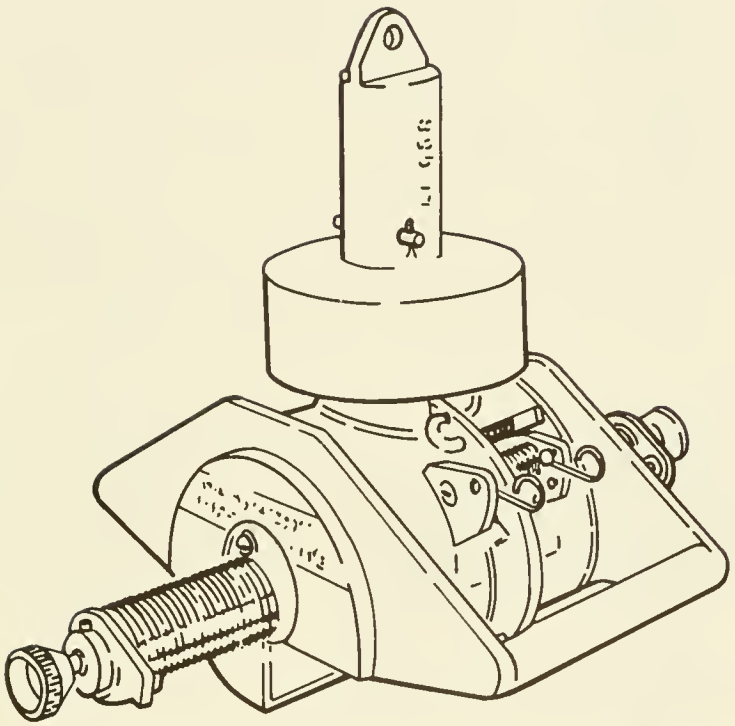

FIG. 6 SHIPEK SEDIMENT SAMPLER

Finish:	International Orange epoxy paint applied over inert primer coat
Sample size:	surface area: 8 in. x 8 in. depth: 4 inches at center
Price:	$900

The Shipek Sediment Sampler is designed for sampling unconsolidated sediment, from soft ooze to hard-puck coarse sand. The device is capable of bringing virtually undistrubed, unwashed samples to the surface from any depth. Basically the unit is composed of 2 concentric half cylinders. The inner semi-cylinder, or sample bucket, is rotated at high torque by 2 helically wound external springs. Upon contact with the bottom it is automatically triggered by the inertia of a self-contained weight upon a sear mechanism. At the end of its 180° travel the sample bucket is stopped and held at the closed position by residual spring torque.

After closure the sample is given optimum protection from washout during the return trip by the cylindrical configuration of the unit. Once on deck, the sample bucket may be disengaged from the rest of the device by releasing two retaining latches at each end of the upper semi-cylinder. The sample is then readily accessible for immediate study or transport to off-site laboratory facilities.

(3) Phleger Corer, Model 840-A
(Hydro Products, San Diego, California) - Fig. 7

Specifications

Weight:	13 1/2 lbs
Valve:	Naval bronze and neoprene
Cutting nose:	Bayonet-detach chromalloy, precision ground
Core barrel:	Steel tubing 25 in. long x 1.5 in. diameter
Core liners:	Clear buterate tubing
Sample size:	24 in. long x 1.38 in. diameter
Unit weight:	25 lbs, less weights; 75 lbs including chest
Sea chest Dimensions:	32 in. x 15 in. x 9.6 in.
Price:	$345

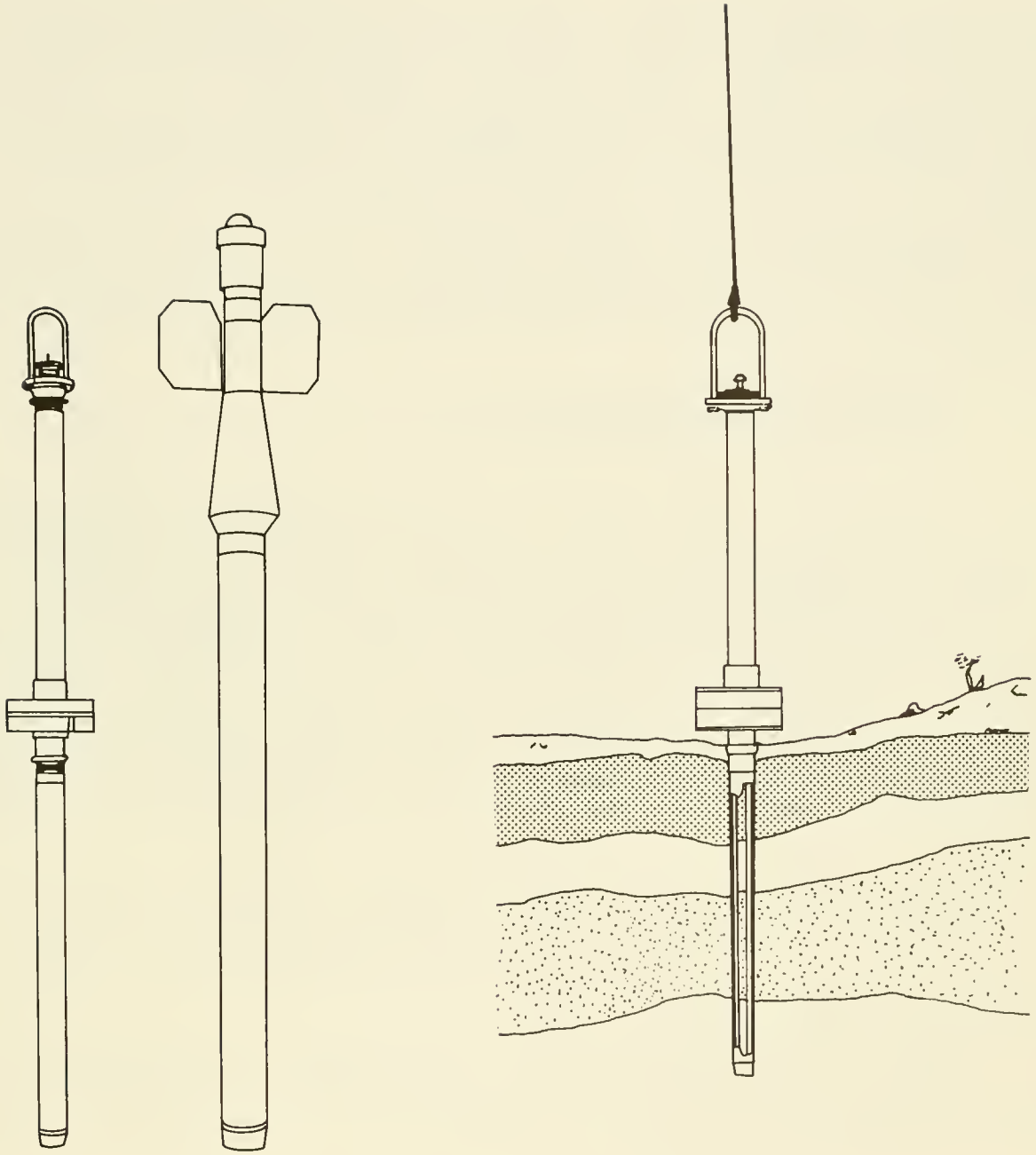

FIG. 7 PHLEGER CORE SAMPLER

The Phleger Corer is a compact, general purpose sampler for obtaining sediment cores. Core retention is accomplished by a simple positive-displacement valve arrangement providing closure of the top of the tube. The resulting vacuum created inside the tube when it is withdrawn from the sediment holds the core securely in the buterate core liner. Little wash out is experienced at the bottom of the sample, and no loss is possible at the top portion of the core. Upon return to the surface, the clear buterate core liner is easily removed from the corer. The liners are replaceable and provide positive support of samplers for permanent storage or for when it is desirable to split the core container for cross-section analysis.

3.2.4 Storage of Sediment Samples

The same principles for the storage of water samples should also be applied to the storage of sediment samples. In addition, attention must be given to the effect of biological activity on the sample characteristics in the sediment samples. The concentrations of micro organic and inorganic components in sediment samples are liable to change rapidly on storage owing to bacterial or enzymatic action. If possible, samples should be analyzed within an hour of collection; if the analysis has to be delayed, they should be placed in glass bottles and immediately frozen with dry ice on board ship. The samples can then be brought back to the laboratory and stored in a deep freeze until analyzed.

IV

DETERMINATION OF EXPLOSION PRODUCTS

4.1 DESIGN OF MEASUREMENT SYSTEM

There are three basic steps in the design of a measurement for characterization of explosion products in water. These are based on the answers to the following questions:

(a) Why are the measurements needed? or
"Objectives of Analysis"

(b) What parameters should be sought? or
"Parameters of Analysis"

(c) How should the measurement be made? or
"Method of Analysis"

4.1.1 Objective of Analysis

The objectives of explosion products analysis are as follows:

(a) Establish the base of information on the present quality of water bodies and sediment in the vicinity of the explosion test area for evaluating future changes in water quality.

(b) Determine the amounts of toxic substances, chemicals, organic substances or solid wastes introduced into bodies of water and sediment immediately after the explosion.

(c) Determine the effects of continued testing at a site in terms of possible long term accumulation of pollutants from the tests.

4.1.2 Parameters for Analysis

The choice of parameters for analysis depends primarily on the type of information sought. It is of vital importance to try to understand the complete problem. The number of tests performed on such samples should be based on the following considerations:

(a) The analysis should produce valuable data and valid conclusions can be drawn from it. Tests should be ruled out if they are insignificant to the objective of the program.

(b) Priority of tests should be established according to their importance, practicality, and cost. Very often part of the tests must be abandoned because of lack of time, equipment, and personnel. Only the more important ones will be processed.

(c) In addition to the tests used for identification of various types of pollutants (e.g. explosion products), nonspecific tests (e.g. pH, temperature, total carbon and turbidity) should also be considered. These tests are frequently used to correlate data in the whole analysis.

The parameters and the nonspecific tests for several explosives are listed in Table 3. These are given as a general guideline. The specific analyses to be performed in a water pollution study will depend on the types of explosive materials used in the test and the objective of the program.

In general, it is more important to measure the potentially harmful products than the harmless ones. However, one that is

TABLE 3

PARAMETERS FOR ANALYSIS

DISSOLVED GASES	DISSOLVED COMPONENTS
HCN	Al
NH_3	Pb
CO	Zr
CH_4	Li
C_2H_6	Nitrate
Cl_2	Chloride
CO_2	Explosives
N_2	SEDIMENT
SUSPENDED SOLIDS	
Al_2O_3	Al_2O_3
PbO	PbO
ZrO_2	ZrO_2
Explosives	Explosives
Total Suspended Solids	Particulate Carbon
Particle Size Distribution	NON SPECIFIC
Particulate Carbon	
	pH
	O_2
	Turbidity
	Temperature

harmless, but easy to measure, can be used as an indicator of the presence of others.

4.1.3 Methods of Analysis

Following the establishment of the objectives of the measurement program and the selection of parameters for analysis, suitable analytical methods are then selected. There are no prescribed procedures which are applicable to all situations but the best method for any given situation must be based upon consideration of many factors. Some of the more important factors are:

(a) Required sensitivity
(b) Accuracy of method
(c) Presence of interferences
(d) Number of samples to be analyzed
(e) Necessity of field or in situ analyses
(f) Speed of analysis required for results
(g) Availability of required instruments
(h) Number and skill of laboratory personnel
(i) Cost of the analyses

Listings of "standard" and "recommended" analytical methods for natural waters and marine waters are to be found in a variety of publications.

For this report a literature survey of these methods was conducted. Based upon the above considerations, the most appropriate procedures were selected, refined, combined, and evaluated to establish their applicability to the analysis of explosion products. General discussion of the methods will be given and specific analytical procedures for some explosion products will be presented.

4.2 SPECIFIC CONSIDERATIONS

4.2.1 Fresh Water vs Seawater

Most of the analytical methods used in water analysis can be applied to fresh water as well as seawater. However, the complexity of seawater often causes a number of problems in trace analysis in that medium:

1. The larger quantity of salts present in seawater reduces the efficiency of some separation techniques, such as ion exchange and solvent extraction.

2. Many conventional techniques used for the measurement of trace elements in water are complicated by the interference of the overwhelming quantity of dissolved ions present in the seawater matrix.

3. In seawater trace elements may exist in many different complex species which could give erroneous results in analytical determinations if the method employed is dependent of the chemical states of the trace elements.

Consequently, many conventional analytical techniques for analysis of trace elements in water cannot be directly applied to seawater solutions. Therefore, selection of special procedures are necessary.

4.2.2 In-situ Analysis

It is practically impossible to handle and process a water sample without changing its characteristics. The best chance for an error-free procedure lies in the use of in-situ analyses. In-situ analysis not only alleviates the problems of sampling, sample transportation, and storage but also provides analyses continuously or at short time intervals on a 24 hour basis. The excellent coverage of fluctuations in water quality by the continuous monitoring systems will often need to be coupled with sampling programs to define the types of pollutants being introduced and their dispersion characteristics.

A number of systems are commercially available which are designed to automatically measure and record water quality parameters by instrumental methods of analysis. These systems are usually capable of measuring temperature, conductivity, dissolved oxygen, turbidity, pH, and chloride. Certain parameters are measured for specific applications, e.g., the monitoring of fluoride, chlorine, nitrates, cyanides, and copper in certain waste effluents.

Although in-situ analysis offers a number of advantages, its use is still limited by the following reasons:

1. The cost of instruments and supporting equipment for the in-situ analysis is relatively high compared to laboratory analysis.

2. Analyses cannot be repeated because no sample is collected.

3. Problems in sensitivity, interference, and accuracy often make in-situ analysis unreliable and impractical.

4. Trained analysts must be at the site to perform or supervise the analyses.

In view of the above limitations, it is recommended all the analyses for the explosive test program to be performed in the laboratory with the exception of some parameters, (e.g. temperature, turbidity, and dissolved oxygen), which require in-situ measurements.

4.2.3 Concentration and Separation

Many current methods of water analysis do not permit the direct determination of elements at low concentrations because of limits of detectability by certain analytical instruments and because of interferences from other constituents in the sample. This is particularly true for seawater analysis, which, as previously discussed, presents many difficulties in the direct determination.

Before the determination can be made, it is usually necessary to concentrate the trace element from a large volume of water. After concentration, the element is separated, where necessary, from other elements which may also be removed by the concentration procedure, and determined by a specific and sensitive physico-chemical method.

Concentration and separation techniques have been discussed in the literature.[11,12,13] A summary of these techniques is presented in Table 4.

Although these various separation and concentration techniques are useful and frequently required, they do introduce another step into the analytical process. The procedures involved often are time-consuming and there always exists a possibility of contamination introduced by the reagents and the manipulation used in the procedures. Thus, wherever possible, interferences should be removed by masking

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[11] Spencer, D. W. and Brewer, P. G., "Analytical Methods in Oceanography, I. Inorganic Methods", Crit. Rev. Solid State Sci., 1, 409 (1970).

[12] Andelman, J. B. and Caruso, S. C., Handbook of Water and Water Pollution, L. L. Ciaccio, Ed., Vol. 1, Chapter 13, p. 213, Marcel Dekker, New York, 1965.

[13] Berg, E. W., Physical and Chemical Methods of Separation, McGraw-Hill, New York 1963.

TABLE 4

CONCENTRATION AND SEPARATION TECHNIQUES
FOR WATER ANALYSIS

Technique	Application
Freeze Drying	organic materials, inorganic ions
Carbon Adsorption	organic materials
Solvent Extraction	organic and inorganic ions
Ion Exchange	organic and inorganic ions
Cocrystallization	trace elements in seawater
Cooprecipitation	trace elements in seawater
Gas-liquid Chromatography	volatile materials, dissolved gases
Thin Layer Chromatography	organic materials
Membrane Filtration	suspended and particular matter
Centrifugation	suspended and colloidal matter

techniques, or a sufficiently sensitive analytical procedure chosen to eliminate the need to concentrate.

4.3 PROCEDURE

4.3.1 Dissolved Gases

4.3.1.1 Gas Chromatographic Methods

The gas chromatographic approach has been recognized as one of the best methods for the determination of dissolved gases in water. The method provides rapid and accurate measurement, and data may be collected easily and routinely on shipboard. The method consists of stripping the dissolved gases from the test solution with an inert gas and subsequent separation and detection by gas chromatography.

Stripping is essentially a gas-liquid extraction procedure in which an inert carrier gas is bubbled through a sample to carry off the dissolved gases for further separation, concentration, or detection. Gas transfer efficiency in such systems is dependent on the gas-liquid interfacial area and on the degree of mixing.

Gas-exchange separation can be carried out as either a batch or a continuous flow process. In one design, a continuous mixed stream of sample and carrier gas is forced through an aspirator nozzle under 50 pounds of pressure.[14] In another design, the dissolved gases are stripped from the test solution by multiple spinning discs rotating at high speed.[15]

The gas stream from the exchange unit is then passed through the gas chromatographic columns. After the chromatographic separation of the different components, the gas stream is passed through the detector cells (thermal conductivity or flame ionization) and the elution curve is recorded by a strip-chart recorder.

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[14] Dixon, W. S., "Pollution Control by Continuous Dissolved Oxygen Analysis and Associated Instruments", Proc. Water Quantity Measurement and Instrumentation, Technical Report, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio (1960).

[15] Swinnerton, J. W., Linnenbom, V. J., and Cheek, C. H., "Dissovled Gases in Aqueous Solution by Gas Chromatography", Anal. Chem., 34, 483 (1962).

A system based on this method has been developed by Swinnerton et. al[15, 16] for the analysis of CO, CH_4, N_2, O_2, and CO_2 in seawater. The equipment consists of an all-glass sample chamber in which the dissolved gases are stripped from solution by an inert carrier gas (such as helium), a four-way by-pass valve, a commercially available gas chromatograph, and a recorder. The stripped gases are dried and passed to a gas partitioner consisting of two columns. The first (a 6 ft. x 1/4 in. column of 30% hexamethylphoramide on 60-80 mesh column pack) separates CO_2 from the mixture while the second (a 4 ft. x 1/4 in. column of 60-80 mesh column pack followed by a 7 3/4 ft. x 1/4 in. column of 40-60 mesh molecular sieve 13x) resolves the O_2, N_2, CH_4, and CO. A thermal conductivity detector is used to determine the separated gases. A schematic of the system is shown in Fig. 8. The system is calibrated using determinations on water saturated with pure gases at a known temperature and pressure. Sensitivities as low as 0.05 ppm in 30 ml samples can be obtained. A chromatogram of a dissolved gas mixture in water is shown in Fig. 9.

Swinnerton and Linnenbom[17] have develop an extremely sensitive gas chromatographic procedure for the determination of very low concentrations of low molecular weight hydrocarbons in seawater (C_1-C_4). The hydrocarbons are stripped from about 1 liter of seawater with helium and after drying, collected in a series of two cold traps. The first cold trap is a column of activated alumina at -80°C (acetone-dry ice bath) which traps the C_2-C_4 hydrocarbons. The second is a column of activated charcoal, at -80°C, which traps the methane. Following a stripping period of 15 to 20 minutes the temperature of the cold traps is raised to 90°C and the gases back flushed with helium, from the traps into the gas chromatograph. The methane is passed through a 4 ft. x 1/4 in. column of silica gel while the C_2-C_4 hydrocarbons are resolved by either a 4 ft. x 3/16 in. activated alumina column with 10% paraffin oil or a 10 ft. column of chromosorb with 20% SF-96 (or SE-30) depending on whether

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[15]Swinnerton, J. W., Linnenbom, V. J., and Cheek, C. H., op cit, pg 37

[16]Swinnerton, J. W., Linnenbom, V. J., and Cheek, C. H., "Revised Sampling Procedure for Determination of Dissolved Gases in Solution by Gas Chromatography", Anal. Chem., 34, 1509 (1962).

[17]Swinnerton, J. W., Linnenbom, V. J., and Cheek, C. H., "Determination of the C_1 to C_4 Hydrocarbons in Seawater by Gas Chromatography", J. Gas Chromatog., 5, 570 (1967).

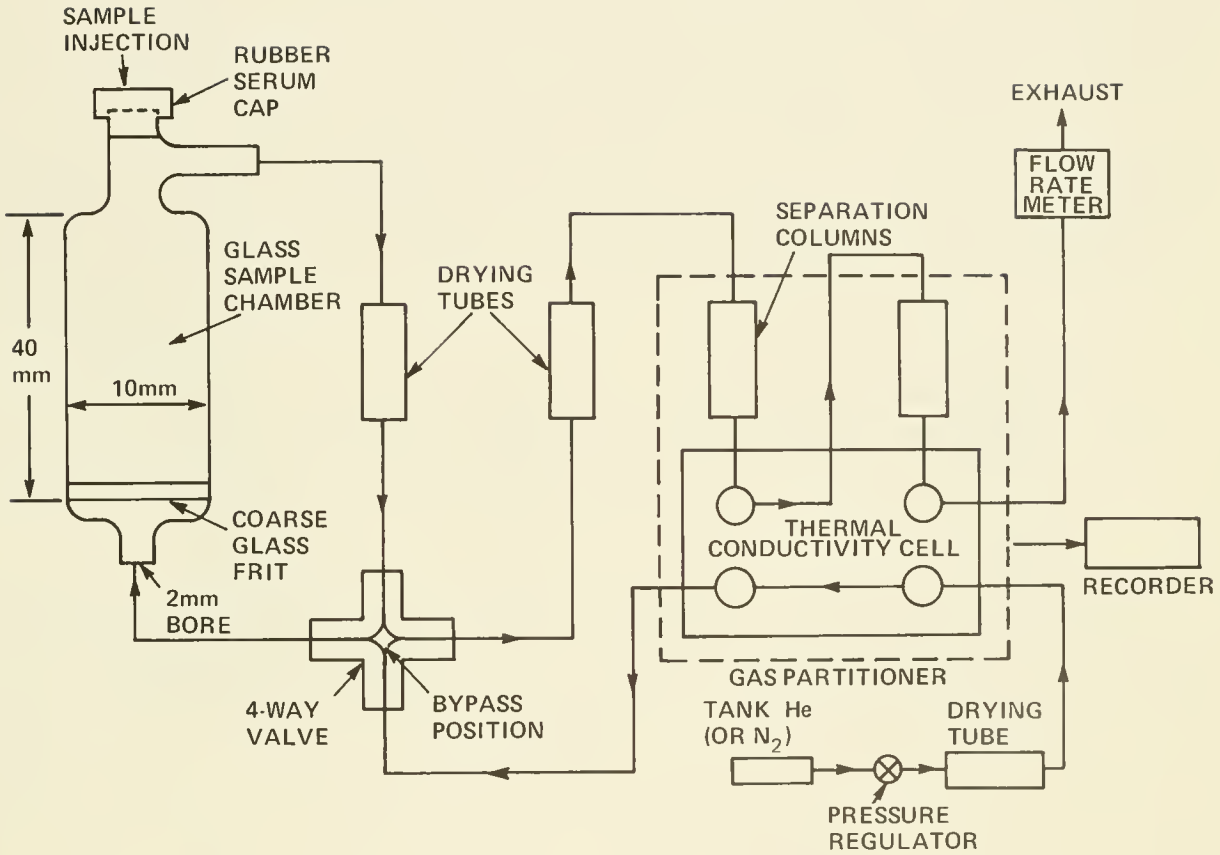

FIG. 8 SCHEMATIC DIAGRAM OF SYSTEM FOR DISSOLVED GAS ANALYSIS

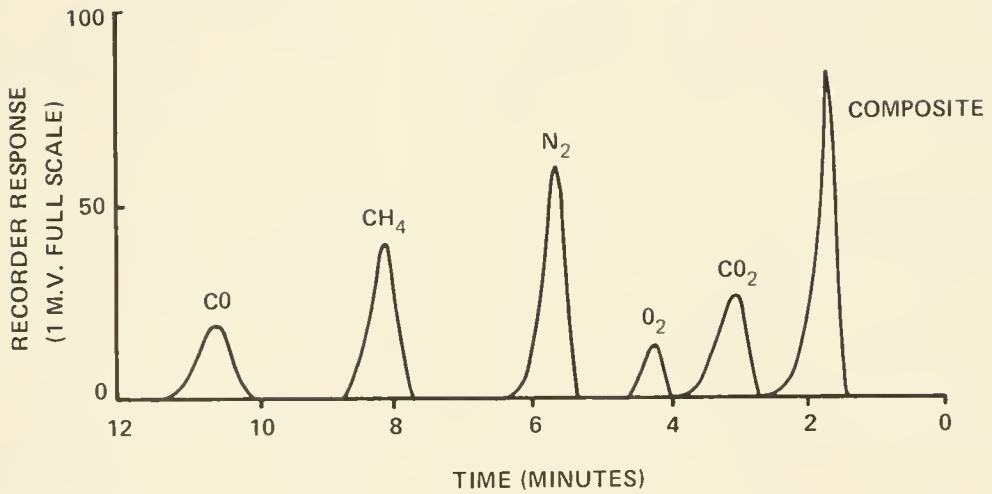

FIG. 9 CHROMATOGRAM OF DISSOLVED GAS MIXTURE IN WATER

resolution of the higher or lower molecular weight olefins from normal paraffins is desired. A flame ionization detector is used and calibration is with gas saturated distilled water. The system is shown in Fig. 10.

The sensitivity of the system is about 5×10^{-10} ml/l with a precision of $\pm$ 10%. The procedure can also be used for the determination of very low concentrations of carbon monoxide. The carbon monoxide, stripped from the seawater, is trapped in a column of one quarter activated charcoal and three quarters molecular sieve at -77°C. The gas is back flushed from the cold trap by raising the temperature to 90°C and separated by the silica gel column. Before passing to the flame ionization detector, hydrogen is introduced and the carbon monoxide quantitatively reduced to methane by passing through a heated tube containing nickel catalyst supported on 30-60 mesh silocel firebrick.

The time required for analyzing 1 liter of seawater for CO, methane, and other light hydrocarbons is approximately 45 min. The complete system costs approximately $10K. The cost for analyzing the dissolved gases is estimated to be $100 per sample.

Precaution must be exercised about doing dissolved gas analysis by shipping water samples from the point of collection to a laboratory for analysis.[18] Methane is probably the most stable gas, but it can be produced or consumed by various organisms. Carbon monoxide and ethane can be affected by presence of bacteria and by the breakdown of dissovled organic matter in the samples. Samples should be treated with sodium azide (which destroys marine bacteria) and kept in a cool dark place. There will most certainly be an air bubble at the top of the water sample when it finally arrives at the laboratory. This will be the result of degassing due to the changing temperature and agitation of the water sample. To be sure of the gas concentration in the water, this air bubble must be analyzed.

4.3.1.2 Specific Ion Electrodes

Two dissolved gases in the explosion products, NH_3 and HCN, can be conveniently measured by specific ion electrodes. Specific ion electrodes are basically potentiometric membrane electrodes systems which operate on a principle similar to that of the glass electrode for the measurement of pH. The experimental procedure in

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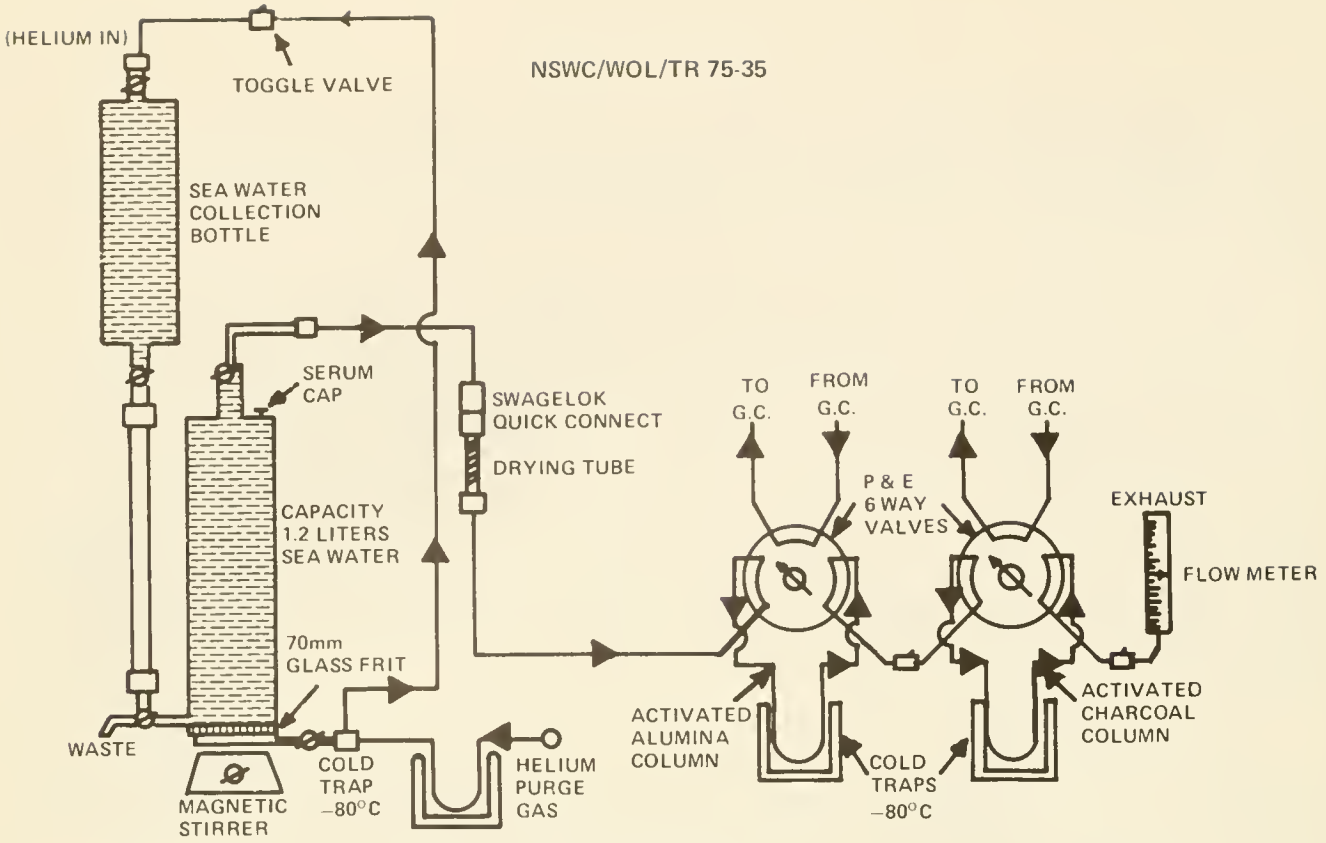
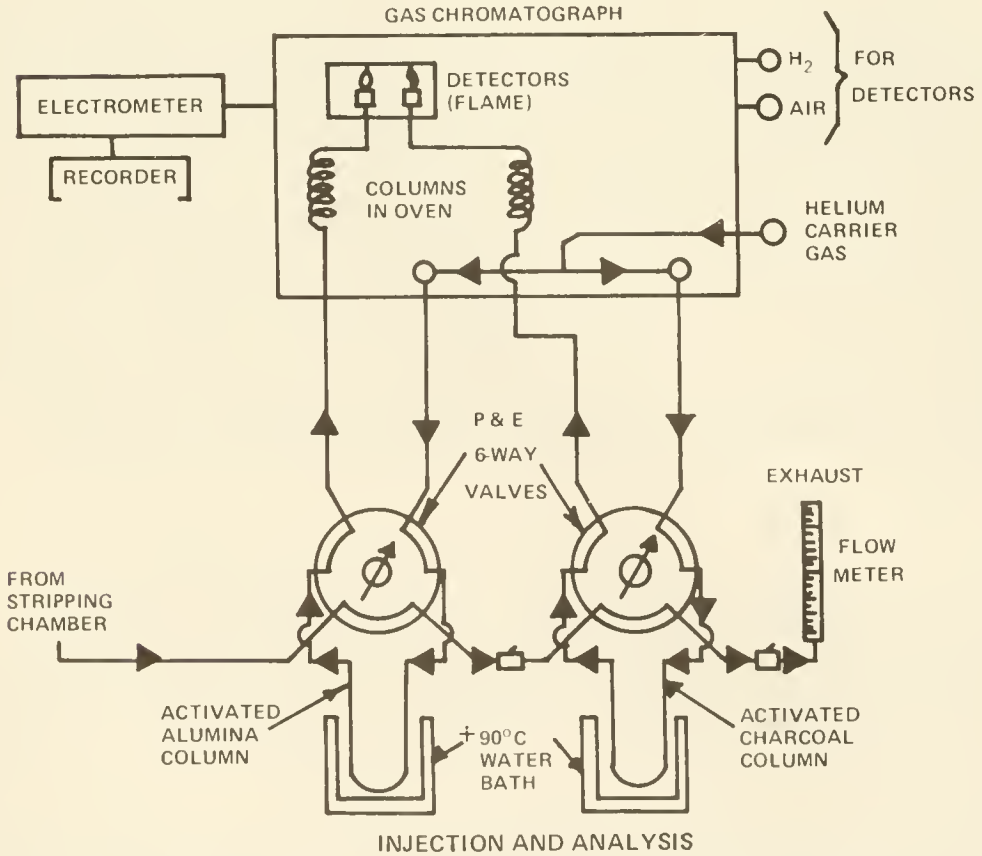
[18] Lamontagne, R. A., Naval Research Laboratory, Private Comm. (1974).



SAMPLING AND STRIPPING



INJECTION AND ANALYSIS

FIG. 10 DIAGRAM OF SYSTEM FOR HYDROCARBON DETERMINATION

their use is also quite similar to that for the glass pH electrode. They are used with a reference electrode, such as saturated calomel or silver-silver chloride, and a high impedance potential measuring device, such as a pH meter with a millivolt scale. A calibration plot of voltage versus the logarithm of concentration of the test ion is made, generally for at least a 10-fold range of concentration. The voltage for the test solution is measured, and the test ion concentration is then calculated from the calibration plot. For on-the-spot, plant or field measurements, a portable, direct-reading specific ion meter is used (Orion Series 400 specific ion meters).

The major advantages of specific ion electrodes for use in water analyses are their speed and ability to be used for in-situ monitoring. Minimal sample and reagent preparation prior to analysis are required. The method also offers a wide concentration range, and a precision and accuracy comparable to other accepted methods. The system is relatively inexpensive. A portable, direct-reading specific ion meter costs $450 and prices of individual specific ion electrodes range from $150 to $300. The cost for analysis is approximately $10 per sample.

a. Ammonia

The use of an ammonia specific ion electrode in the determination of ammonia in surface waters, sewage samples, and saline waters has been recently developed.[19] The electrode is an Orion Model 95-10 gas sensing electrode, incorporating an internal reference electrode and a diffusion-type membrane.

Dissolved ammonia from the sample diffuses through a highly gas-permeable membrane until a reversible equilibrium is established between the ammonia level of the sample and the internal filling solution. Hydroxide ions are formed in the internal filling solution by the reaction of ammonia with water,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The hydroxide level of the internal filling solution is measured by the internal sensing element and is directly proportional to the level of ammonia in the sample. The electrode potential is

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[19]Thomas, R. F. and Booth, R., "Selective Electrode Measurement of Ammonia in Water and Wastes", Environ. Sci. Technol., 7, 523 (1973).

essentially Nernstian with respect to the ammonia level and approximately follows the equation:

$$E = Eo - S \log (NH_3)$$

E = electrode potential in millivolts

Eo = approximately 180 mv (varies slightly from electrode to electrode)

S = the Nerst slope, 58 mv/decade at 29°C

The ammonia electrode is almost totally interference free. Anions, cations, and common gases (carbon dioxide, sulfide, cyanide, and sulfur dioxide) do not interfere. Sample color, turbidity, and the presence of suspended solids do not affect the measurement. Used with an expanded scale pH/mv meter, the electrode is capable of precision equal to the best colorimetric methods for ammonia. The sensitivity is approximately 10^{-6} moles/liter (20 ppb).

b. Cyanide

The cyanide specific ion electrode has been used for rapid, direct measurement of cyanide ions in waste waters.[20] The cyanide electrode uses a membrane of silver sulfide and silver iodide. Cyanide ion in the sample reacts with the silver iodide in the membrane to release iodide into the solution. The iodide at the membrane surface is proportional to the level of cyanide and is in turn sensed by the electrode:

$$2CN^- + AgI \longrightarrow Ag(CN)_2^- + I^-$$

As a consequence the electrode responds to cyanide with Nernstian behavior:

$$E = Eo + S \log(CN^-)$$

where S is the electrode slope (about 59 mv for a ten-fold increase in the cyanide level at 25°C). The lowest level of cyanide that can be measured is about 50 ppb.

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[20] Riseman, J. H., "Electrode Techniques for Measuring Cyanide in Waste Waters", Am. Lab., 4, 63 (1972).

Cyanide can be present as free cyanide ion and as dissolved HCN gas. The cyanide electrode responds only to the free cyanide ion, so the sample must be adjusted to the corrected pH range before measurement.

Sample pH adjustment before measurement is effected by adding concentrated NaOH to the sample to make it 0.1 M in hydroxide ion. This will make the sample pH about 13, insuring that substantially all the HCN is converted to free cyanide ion. A calibration curve for the cyanide electrode is made using a series of standardizing solutions of different concentrations. Each standard solution is made 0.1 M in hydroxide ion so that the NaOH treated samples and standards will have about the same ionic strength and pH.

The electrode does not respond to most common ions in water, such as fluoride, chloride, nitrate, sulfate, phosphate, carbonate, sodium, potassium, and ammonium. Sulfide and iodide ions are the only major interferences.

4.3.1.3 Colorimetric Method

Chlorine in water may be present as free available chlorine (in the form of hypochlorous acid and/or hypochlorite ion) or as combined available chlorine (chloramines and organic chloro derivatives). Chlorine in aqueous solution is not stable, and the chlorine content of samples, particularly weak solutions, will rapidly decrease. Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine present in such solutions. Therefore, it is recommended that chlorine determinations be started immediately after sampling, avoiding excessive light and agitation.

Several methods have been described for the determination of free or combined available chlorine in water.[21] The colorimetric method using orthotolidine appears suitable for field use. In this method, the water sample is mixed with a 2N HCl solution containing 0.15% orthotolidine (the ratio by weight of orthotolidine to chlorine must be at least 3:1). A yellow holoquinone color is developed, and the color intensity is immediately measured with a portable colorimeter (Hach Chemical Co., Ames, Iowa; Model DR-EL, $330). The minimum detectable concentration of chlorine is approximately 10 µg/l.

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[21] Standard Method for Examination of Water and Wastewater, 1971, 13th Edition, American Public Health Association, Washington, D. C.

4.3.2 Dissolved Constituents

4.3.2.1 Metallic Ions

Determination of metallic ions in water from the dissolved explosion products can be accomplished by many methods. A recent study shows that atomic absorption appears to be the best technique for the analysis of trace metals in marine waters.[22] The method is simple, rapid, and applicable to a large number of metals in surface waters, domestic and industrial wastes, and saline waters.

However, the concentration of the metals in the water samples may be below the practical limits of detection by atomic absorption (Table 5). Although the recently developed graphite furnace technique has increased the limits of detection by several orders of magnitude, severe problems have been encountered in the direct analysis of trace metals in seawater with this technique. Therefore, when trace metals are present in low concentration, they must be concentrated in some manner before analysis by atomic absorption analysis (see Section 4.2.3).

Table 5

SENSITIVITY OF ATOMIC ABSORPTION

Metal	Toxicity Limit* (mg/l)	AA Sensitivity** (mg/l)	Optimum Concentration Range (mg/l)
Al	1.5	1.0	10-50
Pb	0.03	0.5	4-20
Zr	N.A.	10	100-800
Li	N.A.	0.035	0.4-2

*The maximum permissible concentration in water without constituting a hazard in the marine environment.

**The concentration that produces an absorption of 1%.

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[22] Lai, M. G., "Evaluation of Analytical Techniques for the Determination of Trace Elements in Marine Waters", Naval Ordnance Laboratory, NOLTR 74-116, 24 July 1974.

a. Sample handling

For the determination of dissolved constituents the sample should be filtered through a 0.45μ membrane filter as soon as practicable after collection. Acidify the filtrate with 1:1 HNO_3 (3 ml per liter). Normally this amount of acid will lower the pH to 2 or 3 and should be sufficient to preserve the sample indefinitely.

b. Concentration

Aluminum

A method for the concentration of Al in water has been developed by Hsu and Pipes.[23] In their method, a benzene solution of diphenylthiocarbazone (0.1% by wt.), 8-quinolinol (0.75% by wt.), and acetylacetone (20% by vol.) is used to extract Al from water. The optimum pH for extraction is about 5. An extraction ratio as high as 200 (1000 ml aqueous sample and 5 ml benzene solution) can be conveniently used. A sensitivity of 9 μg/l can be attained by this method.

Lead

A procedure has been developed by Brooks et al for the extraction of Pb from saline waters.[24] The procedure should be applicable to fresh waters as well. In the procedure samples of seawater (750 ml) are placed in 1000 ml Erlenmeyer flasks and 35 ml of methyl isobutyl ketone (MIBK) are added to each flask followed by 7 ml of 1% ammonium pyrollidine dithiocarbomate (APDC) solution. The samples are then equilibrated for 30 min. on a mechanical shaker. The phases are separated by means of a separatory funnel and the organic phases are stored in polyethylene bottles. With this procedure a sensitivity of 2 μg/l can be attained.

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[23] Hsu, D. Y. and Pipes, W. O., "Modification of Technique for Determination of Aluminum in Water by Atomic Absorption Spectrophotometry", Environ. Sci, Technol., 6, 654 (1972).

[24] Brooks, R. R., Presey, B. J., and Kaplan, I. R., "APDC-MIBK Extraction System for the Determination of Trace Elements in Saline Waters by Atomic-Absorption Spectrophotometry", Talanta, 14, 809 (1967).

Lithium

Lithium in seawater may be directly determined by atomic absorption without separation and concentration.

Zirconium

Any zirconium introduced into the natural waters will be rapidly hydrolyzed at the pH of the waters (seawater and fresh water) to a colloidal hydrous oxide which will be readily precipitated. Therefore, the concentration of soluble Zr is expected to be extremely low. The co-precipitation technique with iron hydroxide at a pH of 9.0 to 9.5 described by Slowey et al[25] is used for the concentration of Zr in water. Each sample previously filtered through 0.45μ filter is co-precipitated three times by the addition of 12 mg of Fe^{+3} per liter of sample. The pH is then adjusted to 9 by the addition of ammonium hydroxide. The sample is filtered through Millipore filters. The precipitate is dissolved in 9N HCl and the iron extracted with diisopropylether. The sample is then evaporated to almost dryness and diluted to 10 ml with 2% HF. With this procedure a sensitivity of 0.1 ppm can be attained.

Direct analysis of metals by atomic absorption generally costs $15 per element. The cost will increase several times if concentration procedures are required.

4.3.2.2 Explosives

Very few reliable methods for the analysis of explosives at low concentration (parts per million) in water and in sediment have been developed. Procedures for several common types of explosives (TNT, RDX, Tetryl, and ammonium perchlorate) were established by Hoffsommer et al at NAVSURFWPNCEN based on the use of gas chromatography and the ion specific electrode.[26] A method for the analysis of HMX in water

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[25] Slowey, J. F., Hayes, D., Dixon, B. and Hood, D., "Distribution of Gamma Emitting Radionuclides in the Guld of Mexico", Symposium on Marine Geochemistry, University of Rhode Island, Occasional Publication No. 3, Aug 1965.

[26] Hoffsommer, J. C., Glover, D. J., and Rosen, J. M., "Analysis of Explosives in Sea Water and in Ocean Floor Sediment and Fauna", Naval Ordnance Laboratory, NOLTR 72-215, 11 Sept 1972.

was also developed based on the thin-layer chromatography.[27] Methods for the analysis of any other explosives used in the underwater explosion program would have to be developed.

TNT, RDX, Tetryl

A 100-ml water sample is extracted with 30 to 40 of benzene; the benzene is evaporated to a small volume and injected into a gas chromatograph equipped with a high temperature nickel-63 electron capture detector. Chromatographic traces of the water extracts are compared to chromatographic traces of standard solutions of TNT, RDX, Tetryl. Retention times and areas of peaks are measured by means of an automatic digital integrator to an accuracy of $\pm$ 1 sec. for retention time and an integration area count of approximately 9 counts/mm^2. Detection levels for TNT, RDX, and Tetryl have been determined to be 2, 5, and 20 parts per trillion, respectively, under normal routine working conditions.

HMX

A 100-ml water sample is extracted with four 25-ml portions of benzene. The combined benzene extracts are evaporated under reduced pressure (17 mm/20°C) with a water aspirator to dryness. The residue is taken up in 1.0 ml of acetone. A total of 20- l are spotted in four 5- l portions as one spot with drying between spotting onto a 0.3 mm silica gel HF-254 thin-layer glass plate. Standard solutions of HMX are similarly spotted to the right and to the left of the unknown, and the thin-layer plate is developed in an ascending manner with benzene/acetone, 4:1, as eluent. After air drying, the TLC plate is placed in a ultraviolet cabinet, and zones for HMX are located as dark spots under 254 mm radiation.

In order to determine the HMX present, the dark areas are marked with a needle and photographed with a polariod camera with transparency film. The developed film is projected by means of a lantern slide projector onto a sheet of white paper 3 to 4 feet away, and the area for the HMX spots traced with a pencil. The standard and sample area are measured by means of a precision planimeter. The weight of HMX in the unknown spot is calculated from the following:

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[27] Glover, D. J. and Hoffsommer, J. C., "Thin-Layer Chromatographic Analysis of HMX in Water", Bull. Environ. Contaim. Texicol. 10, 302 (1973).

$$\text{Log wt}_{HMX} = \left(\frac{\text{log wt STD-1} - \text{log wt STD-2}}{A^{\frac{1}{2}}_{STD-1} - A^{\frac{1}{2}}_{STD-2}}\right)\left(A^{\frac{1}{2}}_{HMX} - A^{\frac{1}{2}}_{STD-1}\right) + \text{log wt STD-2}$$

A = the area of the respective spots.

Ammonium Perchlorate

The analytical procedure for the determination of ammonium perchlorate is based on the use of a specific ion electrode which develops a potential across a thin porous inert membrane.

The potential measured is a function of perchlorate concentration. A reference curve is prepared using a standard seawater to which is added known amount of perchlorate. Differences in seawater samples may contribute to a small uncertainty in the measurement, particularly at low concentrations. For clear seawater, the method gives satisfactory results in the 1 ppm range, using a research pH meter.

4.3.2.3 Nitrate

The nitrate electrode allows nitrate to be quickly and easily determined in fresh waters. However, the nitrate electrode will not operate in the presence of high levels of other ions, so it cannot be used to measure nitrate in concentrated salt samples such as seawater.

Nitrate can be reduced to ammonia, allowing the ammonia electrode to be used for nitrate analysis, without interference. The reduction procedure is as follows:

1. Place in a round-bottom flask 100 ml of (neutral) sample and a magnetic stirring bar. To the sample, add 1 ml of concentrated HCl and about one-half gram of NaF. Stir vigorously. Add about 0.1 g of finely divided aluminum powder. Wait until the evolution of hydrogen stops, then add 1 ml of 10 M NaOH. Pour the contents into a beaker and measure the ammonia concentration by the ammonia electrode (see 4.3.1.2).

Samples which may already contain ammonia must be measured first. The background level of ammonia is subtracted from the value found after reduction.

The above method will give better than 90% conversion of the sample nitrate. It is recommended that a recovery study be used to determine the conversion efficiency in the type of sample being measured.

4.3.2.4 Chloride

Two methods are presented for the determination of chlorides. The colorimetric method is suitable for use in clear samples with relatively low chloride concentration, and the potentiometric method is suitable for colored or turbid samples with high chloride concentration.

In the colorimetric method, chloride is determined by reacting the sample with mercuric thiocyanate which forms unionized mercuric chloride and thiocyanate ions. The thiocyanate is reacted with ferric ion producing highly colored ferric thiocyanate proportional to the chloride in the original sample.

$$2Cl^- + Hg(SCN)_2 \longrightarrow HgCl_2 + 2SCN^- \xrightarrow{Fe^{+3}} Fe(SCN)^{+2}$$

The color intensity is then measured with a spectrophotometer at a wavelength of 480 mm. There are no significant interferences in the analysis.

In the potentiometric method, chloride is determined by potentiometric titration with silver nitrate solution using a glass and silver-silver chloride electrode system. During titration, an electronic voltmeter is used to detect the change in potential between the two electrodes. The end point of the titration is that instrument reading at which the greatest change in voltage has occurred for a small and constant increment of silver nitrate added.

Ferric ion interferes if present in an amount that is substantially higher than the amount of chloride. Chromic ion, ferrous iron, and phosphate do not interfere. Iodide and bromide also are titrated as chloride.

Grossly contaminated samples usually require pre-treatment. Where contamination is minor, some contaminants can be destroyed simply by the addition of nitric acid.

4.3.3 Suspended Solids

4.3.3.1 Suspended Metals

For the determination of suspended metals a representative volume of sample should be filtered through a 0.45μ membrane filter. Transfer the membrane filter containing the particulate matter to a beaker and add 3 ml of HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot-plate and digest the material. When the acid has evaporated, cool the beaker and add another 3 ml of HNO_3. Cover and continue heating until the digestion is complete. Add 1:1 HCl (2ml) to the dry residue and again warm the beaker to dissolve the material. Filter the sample to remove silicates and other insoluble material. The sample is now ready for analysis by atomic absorption.

4.3.3.2 Suspended Explosives

A representative volume of sample is filtered through a 0.5μ solvent-resistant filter (membrane or glass fiber). The particulate matter collected on the filter is washed with several small portions of benzene which is drawn through the filter after each washing. The combined benzene extracts are analyzed for explosives using procedures described in Section 4.3.2.2.

4.3.3.3 Non-filterable Solids

a. Total Non-filterable Solid

Total non-filterable solids are defined as those solids which are retained by a standard membrane filter and dried to constant weight at 103-105°C.

A known volume of sample is passed through a weighed filter (0.8μ). The filter is carefully removed from the filter funnel assembly, placed in a drying oven, and dried at 103-105°C to constant weight.

b. Particle Measurement

Particle measurement of the suspended solids can be made by manual microscope methods, but they are tedious and time consuming. Other indirect measuring techniques such as light scattering, sedimentation, and electrical field effect are limited by lack of precision. A recently developed Millipore IMC System (Millipore

Corp., Bedford, Massachusetts) offers both speed and precision in counting particles, in determining size distributions and in characterizing shapes. It can rapidly and accurately measure such parameters as diameter, longest dimension, or area.

Samples for TMC measurement are prepared by Millipore filtration. This results in a random distribution of particles. The filters are made transparent with various clearing techniques and mounted on glass slides. The sample is ready for measurement.

The sample is placed on the microscope stage and the illumination and focus are adjusted while the operator is viewing the sample. The camera scans the microscope image and converts its contents into a video signal which is sent to the computer. The computer receives the video signal and applies the logic necessary to count and measure particles in the field of view. The video signal then goes to the viewing monitor where the field of view is reconstructed. Measurements are displayed instantly in micrometers or square micrometers and can be made on individual particles as well as entire fields of view.

4.3.3.4 Particulate Carbon

To determine the particulate carbon in water a Dohrmann total organic carbon analyzer (Envirotech Corp., Santa Clara, Calif., $8,000) can be used. In the analysis a 30µl acidified water sample is injected into a sample boat containing an oxidizer at room temperature. The boat is then advanced to the 90°C vaporization zone where H_2O, CO_2 (from dissolved CO_2, carbonates and bicarbonates) and organic carbon materials which are volatile at 90°C are swept into the by-pass column. Here volatile organic carbon (VOC) is trapped on a Porapak Q column at 60°C while the H_2O and CO_2 are swept through the switching valve and vented to atmosphere.

After sample vaporization, the valve is automatically switched to the pyrolyze position and the boat is then advanced to the pyroysis zone. Residual organic carbon (ROC) materials left in the boat react with the oxidizer at 850°C to produce CO_2. At the same time the by-pass column is backflushed at 120°C thus sweeping the VOC material through the pyrolysis zone. Both the VOC and the CO_2 (from the ROC) are swept by helium into the hydrogen enriched nickel catalyst reduction zone where all carbon is converted to methane at 350°C.

The reduction product is swept through the switching valve, the water detention column and into the flame ionization detector

which responds linearly to methane. The detector output is integrated and displayed in milligrams per liter (mg/l) on the digital meter.

4.3.4 Sediment

4.3.4.1 Metals

Metals in the sediment samples can be determined by a simple procedure essentially described by Iskandar and Keeney.[28] Each sediment sample is mixed thoroughly, and a subsample is dried at 105°C in a forced-air oven. The dried sample after discarding large pebbles, twigs, shells, bugs, etc, is ground with a porcelain mortar and pestle until fine (100-mesh).

A subsample (1-2 grams) is placed in a 70-ml Pyrex digestion tube and predigested at room temperature for 16 hours by reaction with 5-10 ml of concentrated HNO_3. Subsequently, the sample is digested on an hot plate at 120°C for 3 hours. After it is cooled, 3 ml of concentrated $HClO_4$ are added, and the mixture is heated at 210-220°C until HCl fumes are evolved. The cooled digest is then filtered through a 0.45μ Millipore filter and brought to a 25-ml volume with distilled water. The metals in the solution are determined by atomic absorption.

4.3.4.2 Explosives

The analyses of explosives in sediment samples are generally more involved than in water samples. First, the explosives are extracted from the sediment with the appropriate solvent. Then, the explosives in the extract are separated by thin-layer chromatography and finally analyzed by gas chromatography.

TNT, RDX, Tetryl

Seventy-five to 100 grams of the sediment sample are stirred with 50 ml of benzene. The benzene extract is decanted into a 100-ml round-bottom flask for vacuum evaporation.

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[28] Iskandar, K. I., Keeney, D. R., "Concentration of Heavy Metals in Sediment Cores from Selected Wisconsin Lakes", Environ. Sci. Technol., 8, 165 (1974).

After evaporation of the benzene extract under reduced pressure (17-20mm/20°C), the flask is rinsed with 1.0 ml of pesticide quality benzene and transferred to a 5.0 ml test tube. The benzene is again completely removed under reduced pressure. A total of 0.050 ml of benzene is added to the residue and 0.025 ml of this solution are spotted along a narrow band in 5 separated spots onto a ChromAr 500 TLC sheet. Simultaneously, a standard mixture of TNT, RDX, and Tetryl in benzene is spotted to the right of this band, as a guide.

The fluorescent ChromAr sheet is developed in an ascending manner with hexane/acetone:45/5 as eluent. After air-drying the ChromAr sheet for 5 minutes, zones for the standard TNT, RDX, and Tetryl are located as dark spots under 254 mm UV light. Corresponding areas to the left of these standards are cut out and transferred to a 5-ml beaker. These ChromAr discs are extracted 3 to 4 times with a total of 1.0 to 1.5 ml of benzene. The benzene extracts are combined into a 2.0 ml sample tube with a tapered bottom and the benzene completely removed under reduced pressure. A total of 50μ l of benzene is added to the tapered tube together with 5μ l of o-dinitrobenzene (4.5×10^{-10} g/ l) as internal standard. After thoroughly mixing, a 5 to 6μ l injection of this solution is placed into the gas chromatograph. At this point, the procedure follows that reported in Section 4.3.2.2.

HMX

HMX is extracted from the sediment sample by the same procedure used in TNT, RDX, and Tetryl. After extraction HMX is determined by the procedure described in Section 4.3.2.2.

Ammonium Perchlorate

A sediment sample is stirred with distilled water for several hours, after which the sediment is removed using a centrifuge. Ammonium perchlorate in the solution is measured by the specific ion electrode.

4.3.4.3 Particulate Carbon

The particulate carbon in the sediment can be determined with an organic carbon analyzer (Section 4.3.3.4). The sediment sample is first suspended in water, and an aliquot is then withdrawn for the analysis. Samples with sediment and high dissolved solids content pose no problem. However, the analysis is subject to some degree of error if the organic content other than the particulate carbon is relatively high.

4.3.5 Non-specific Measurements

4.3.5.1 Turbidity

The turbidity of a water sample can be measured in a turbidimeter (e.g., Hach Model 2100A Laboratory Turbidimeter, $525), which is a true nephelometer. The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light the higher the turbidity. The readings are made in the Nephelometric Turbidity Unit (NTU).

Samples taken for turbidity measurements should be analyzed as soon as possible. Preservation of samples is not recommended.

The presence of floating debris and coarse sediments which settle out rapidly will give false high readings. Finely divided air bubbles will also affect the results in a positive manner.

4.3.5.2 pH

The pH of most natural waters falls within the range 4 to 9. The majority of waters are slightly basic due to the presence of carbonate and bicarbonate. A departure from the norm for a given water could be caused by the entry of strongly acidic or basic wastes (HCl in the explosion products). pH is the logarithm of the reciprocal of the hydrogen ion concentration in moles per liter. The practical pH scale extends from 0, very acidic, to 14, very alkaline, with the middle value (pH 7) corresponding to exact neutrality at 25°C.

pH can be measured either colorimetrically or electrometrically. The colorimetric method requires a less expensive investment in equipment but suffers from severe interferences contributed by color, trubidity, high saline content, colloidal matter, free chlorine, and various oxidants and reductants.

Electrometrically pH is measured with a pH meter equipped with either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference). A portable pH meter such as the Micro 50 pH meter (Service Tectonics Instrument, Detroit, Michigan, $125) is convenient for field pH measurements.

4.3.4.3 Dissolved Oxygen

Adequate dissolved oxygen (DO) is necessary for the life of fish and other aquatic organisms. The DO concentration may also be associated with corrodibity of water, photosynthetic activity, and septicity. Therefore, it may be desirable to determine the DO in water after an underwater explosion test.

Membrane electrodes of the polarographic as well as the galvanic type have been used for DO measurements in lakes and reservoirs[29] and in estuarine and oceanographic studies.[30] Being completely submersible, membrane electrodes are well suited for analysis in-situ. Their portability and ease of operation and maintenance render them particularly convenient for field applications.

Membrane electrodes provide an excellent method for DO analysis in polluted waters, highly colored waters and strong waste effluents. They are recommended for use, especially under conditions which are not expedient for use of other chemical methods.

Membrane electrodes are commercially available in larger variety. In all these instruments the diffusion current is linearly proportional to the concentration of molecular oxygen in the test solution.

Dissolved organic materials are not known to interfere in the output from dissolved oxygen membrane electrodes, while inorganic salts, reactive gases, and temperature affect the performance of the electrodes.

No specific electrode or accessory is especially recommended as superior. However, one oxygen analyzer which has been in use and found to be reliable is the Y.S.I. Model 54 oxygen analyzer (Yellow Springs Instrument Co., Yellow Springs, Ohio, $535).

4.3.5.4 Temperature, Conductivity, and Salinity

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[29]Weiss, C. M. and Oglesby, R. T., "Instrumentation for Monitoring Water Quality in Reservoirs", American Water Works Association, 83rd Annual Conference, New York, 1963.

[30]Duxbury, A. C., "Calibration and Use of a Galvanic Type Oxygen Electrode in Field Work", Limol. & Oceanogr., 8, 483 (1963).

As theory and experimental data both indicate temperature changes produced in water by explosions are entirely negligible after a few minutes have elapsed. There seems to be no justification for attempting to measure this effect for the purpose of monitoring a test. However, temperature, along with conductivity and salinity, are often needed data for water quality monitoring.

Conductivity is an important water quality test. Also the conductivity and temperature measurements can be used to estimate total dissolved solids. When measuring dissolved oxygen, it is necessary to correct for the salts dissolved in the water. The salinity measurement provides the data necessary to make this correction and is of particular importance in coasted areas.

To facilitate in-situ pollution studies YSI has developed the Model 33 S-C-T Meter ($250) and Probe ($45) for direct measurement of salinity, conductivity, and temperature. The meter is operated as follows:

Estimate total dissolved solids by dropping the unbreakable plastic probe in water, switching to the appropriate conductivity scale and reading the answer directly from 0 to 50,000 mhos/cm. Switch to the temperature scale and read temperature from -2° to +50°C (accuracy: $\pm$0.1°C at -2°C and $\pm$0.6°C at 45°C). Measure salinity as in estuarian environment by dialing the water temperature and switching to the salinity scale for direct, temperature compensated salinity readings from 0 to 40‰ (accuracy: $\pm$0.9‰ at 40‰ and $\pm$ 0.7‰ at 20‰).

V

CONCLUSIONS AND RECOMMENDATIONS

It is desirable to cover every parameter in a water quality monitoring program, if possible. Accurate assessment of the water quality can be conveniently made if sufficient data have been obtained. However, very often complete coverage of the monitoring parameters cannot be achieved because of lack of time, personnel, or funding. Therefore, priority must be established on the parameters needed to satisfy the minimum requirement of the monitoring program and on the number of measurements necessary for a reliable quantitative estimate.

In the chemical monitoring program of explosion products several basic parameters are recommended:

1. Pre-test conditions

In order to make valid comparisons on water quality data before and after an explosion test and after an explosion test and to establish a long-term trend, pre-test conditions of the test environment should be accurately established. Extensive base-line data on water quality should be compiled.

2. Post-test conditions

Explosion products which are expected to have the most adverse effect on the environment should be selected first for measurement. In addition, explosion products which are pertinent to the objectives of the test program should also be examined. Parameters which are relatively unimportant, but their measurements can be made with very little effort, should be considered. If the products are in a fixed ratio, measurements of a product that can be easily obtained, can be used to estimate the quantity of others in the water.

3. Long-term monitoring

Continuous monitoring of water quality at the test site is unnecessary because underwater explosion tests are usually conducted in an unconfined area. Most of the explosion products would have been diluted and carried away by the water current shortly after the explosion. However, periodical examination of the sediment in the vicinity of the test site should be made in order to assess the degree of long-term accumulation of explosion products in the sediment. This would be particularly important in a shallow water site.

The minimum number of samples collected for analyses should be sufficient to fulfill the objectives of the monitoring program. Multiple sampling, necessary for an adequate characterization of the water body, can be reduced to single sampling as a trade off between cost and accuracy. Less expensive analytical methods can be used to substitute the more expensive ones for the similar purpose.

It should be stressed that the collection of water samples from underwater explosion tests presents many special problems. For example, if automatic equipment is placed too close to the explosive, it may be damaged by the shock wave. However, samplers and other devices can be strung in a line down-current. Also, a boat can be used to traverse the pool immediately following the explosion. In general, the time available for the collection of meaningful data is only a few minutes.

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